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AFML-TR-67-319

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CORROSION-RESISTANT CLADDING FOR 7075-T6 ALUMINUM ALLOY

Thomas A. Lowe
Kaiser Aluminum & Chemical Corporation

TECHNICAL REPORT AFML-TR-67-319

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Department of the Air Force
Air Force Materials Lab (AFSC)
Wright-Patterson Air Force Base, Ohio 45433

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Form 1473

(18) (19) AFML-TR-67-319

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(6) CORROSION-RESISTANT CLADDING FOR

7075-T6 ALUMINUM ALLOY

(9) Annual summary rept. no. 1, Jun 66 - May 67,

(10) Thomas A. Lowe

(11) May 67

(12) 27p.

(15) AF 33(615)-3939

(16) AF-7381

(17) 738107

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(401 923)

FOREWORD

This investigation of new cladding candidates for 7075-T6 aluminum alloys was conducted by the Kaiser Aluminum & Chemical Corporation, Spokane, Washington. This report is the first annual summary report on this two-year project. The work was carried out under Contract AF 33(615)-3939. This contract was initiated under Project 7381, "Materials Applications" Task 738107, "Detection, Prevention, and Control of Corrosion". The work is under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with Mr. Fred H. Meyer, Jr. as Project Engineer. The contract period is from 1 June 1966 to 31 May 1968. The manuscript was released by the authors in September, 1967 for publication as a technical report.

This materials program was conducted in the Kaiser Aluminum Company Department of Metallurgical Research, with personnel of the Corrosion Branch participating. Mr. T. A. Lowe is principal investigator.

This technical report has been reviewed and is approved.

W. P. Conrardy

W. P. Conrardy, Chief
Systems Support Branch
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See 1473

ABSTRACT

Corrosion of Alclad 7075 aircraft alloy prompted the Air Force to sponsor an evaluation of different cladding compositions. The objective was to determine if these compositions offered better corrosion resistance than 7072, while providing adequate galvanic protection.

Accelerated corrosion tests indicate that there are registered aluminum alloys that offer an improvement over 7072. Further work is needed to optimize a composition.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

Heat-treatable Al-Zn-Mg-Cu alloys (such as 7075) provide high level mechanical properties, but comparatively low corrosion resistance. Improvement in corrosion performance is generally obtained by cladding the surface with a corrosion-resistant aluminum alloy, which provides galvanic protection.

Alloy 7072, currently used to clad 7075, offers the 7075 core a high order of corrosion protection, but is itself subject to attack. Field corrosion problems on clad 7075 prompted requests by the Air Force Materials Laboratory for an investigation to determine if better cladding alloys existed. Our objectives under this program were to:

1. Find an alloy having improved surface corrosion performance.

2. Determine if the alloy would provide adequate galvanic protection.

3. Study diffusion characteristics of principal alloying elements to determine if some compositions are more sensitive to diffusion than others.

Time restrictions specified by the contract did not allow new cladding alloy developments. We approached the problem by considering Aluminum Association registered alloy compositions as replacements for 7072.

Suggested alloys are listed in Table I. Reasons for their consideration included:

1. 1199 -- high purity (99.99%) aluminum having a high order of corrosion resistance.

2. 5454 and 5457 -- Al-Mg alloys whose magnesium content gives a high order of corrosion resistance in marine environments.

3. 6253 -- a heat-treatable Al-Mg-Si-Zn alloy that offers strength improvement.

4. 7004, 7040 and 7472 -- corrosion-resistant Al-Zn-Mg (Cu-free) alloys which cover a range of alloy content and Zn:Mg ratio, offer various combinations of galvanic protection and improvement in mechanical properties.

5. 7272 -- an Al-Zn alloy offering a higher level of galvanic protection to 7075 than alloy 7072.

Within this group, we hoped to find (a) an alloy with higher surface corrosion resistance than alloy 7072, with no consideration of mechanical properties, or (b) an alloy of equal or slightly poorer corrosion resistance than 7072 that would offer improved strength characteristics to the clad 7075. Greater strength in the cladding alloy would allow a thicker cladding layer and thereby reduce corrosion associated with diffusion of copper from the core alloy to the cladding surface. The increase in cladding thickness could be justified if composite strength was either unaffected or improved.

Scheduled effort was divided into two phases. Phase I consisted of an evaluation of the nine cladding candidates plus alloy 7072, and selection of the more corrosion-resistant compositions to be used in cladding-7075 composites whose evaluation constitutes Phase II.

SECTION II

CONCLUSIONS

There are standard alloy compositions that provide better corrosion resistance as cladding on Alclad 7075-T6 than does 7072 -- the current cladding alloy.

SECTION III

RECOMMENDATIONS

This evaluation indicates that the Al-Zn-Mg (Cu-free) system offers attractive potential for cladding alloys. The specific compositions tested do not offer the optimum cladding characteristics. Further study is suggested to optimize compositions which will provide:

1. Maximum corrosion resistance and adequate galvanic protection, while offering no significant contribution to mechanical properties.

2. Adequate corrosion resistance and galvanic protection, with a significant contribution to composite strength.

SECTION IV

STATUS

The evaluation of all materials scheduled for accelerated testing is complete. Natural environment exposures have been initiated. Work remaining under the contract is the maintenance of samples in exposure and evaluation of those samples after one year.

PHASE I

SECTION V

MATERIALS

Cladding candidate alloys (Table I) were obtained from plant production lots or cast in laboratory facilities. All material was rolled to 0.055-inch thick sheet. Some of the sheet stock was heat treated and aged by a practice employed for 7075-T6 sheet. This practice was to solution heat treat at 900F for 12 minutes, quench in cold water, level roll to flatten (less than 1% cold work) and age 4 hr at 210F + 4 hr at 310F. The remaining portions of these materials were stored for later use as needed in the evaluation of composite performance. A standard production lot of 7075 was obtained for use in all phases of the evaluation.

The chemical analyses of all alloys are given in Table I.

SECTION VI

PROCEDURE

Phase I includes the accelerated corrosion testing and electrochemical study of the various candidates considered for cladding on 7075-T6.

<u>Accelerated Corrosion Tests</u>

Three sample types were used in all accelerated tests:

1. 4-inch by 6-inch flat panels.

2. Lap joints made with two 4-inch by 4-inch candidate panels joined with aluminum rivets (composition given in Table I) to give a 2-inch lap and final assembly size of 4 inches by 6 inches.

3. Joints fastened with cadmium-plated steel fasteners (AN509-10R10 screw).

The lap joint configuration is shown in Figure 1. Triplicates of each sample type were exposed to:

1. Neutral 5% salt spray for 250, 500 and 1000 hours (Ref 1).

2. Cyclic acidified salt spray for ½, 1, 2, 4 and 8 days (Ref 2).

3. Distilled water fog for 500 and 1000 hours with an interim visual examination at 250 hours.

A modified (100-hr) intergranular corrosion test (MIL-H-6088D, para. 4.4.3) was conducted on all candidates. Solution was replaced every 24 hours.

Electrochemical Measurements

Steady-state solution potentials of all cladding alloys and of alloy 7075 were measured in an aqueous solution containing 53 g/l NaCl and 3 g/l H_2O_2 at 25C.

Galvanic characteristics of each cladding-7075 couple were determined by measuring the galvanic current flow between cladding and core with a zero resistance micro-ammeter. (Anode:cathode area relationship was 1:1.) The electrolyte was an aqueous NaCl solution (3% by weight) maintained at 25C. These measurements ceased when polarization occurred.

Evaluation

Panels from all accelerated tests were evaluated by a system which provides a corrosion resistance rating and an appearance rating. This system was originally developed by ASTM Committee B-8 Sub II (Refs 3 & 4). A "corrosion resistance" rating is determined by assessing the per cent of surface area affected by pitting and etching. A weighting factor is applied to the percentages and their total is used to determine a number rating for the panel. Numbers range from 10 (unaffected) to 0 (severe attack).

The number rating can be translated into pit frequency, if desired. Maximum pit depths are measured with a penetrometer to provide a further comparison of attack severity.

This rating system also provides a means of assessing the amount and degree of staining and streaking. Ratings thus derived combine with the "corrosion resistance" number to provide an "appearance" rating. Two numbers, therefore, provide separate assessments of the corrosion resistance and the general appearance. Table II illustrates a sample rating sheet with an example of rating calculations.

Evaluation dealt with the front surfaces of flat panels and only the mating surfaces of the lap joints. Surfaces around fasteners were also examined to determine the extent to which these dissimilar metals affected them.

The ratings thus obtained with each cladding candidate, in each of the accelerated tests, were combined with an appraisal of galvanic characteristics. Those candidates with the highest combined ratings were chosen to be included in Phase II -- the cladding-core composite evaluation.

SECTION VII

RESULTS AND DISCUSSION

Accelerated Corrosion Tests -- Cladding Candidates

Detailed evaluation results for candidates from each of the accelerated tests were presented earlier (Ref 5). An average rating for each alloy was determined from all corrosion resistance and appearance ratings. The total of these averages served as a measure of the corrosion resistance and appearance performance of cladding candidates. Based on these accumulative totals, the most corrosion-resistant alloys (in decreasing order) were 1199, 5457, 7472 and 7004. On the basis of appearance, the best were: (in decreasing order) 1199, 7472, 5457 and 7004. Lap joints were not rated for appearance.

Electrochemical Data

Table II lists the solution potentials of the cladding candidates and of the 7075 core alloy. These represent the alloys in the "-T6 condition". The potentials of all candidates were more electronegative than that of the 7075-T6 core stock.

Current density-time data for each cladding-7075 galvanic couple were obtained in triplicate. Representative of these data for all couples are the curves shown in Figure 2 for the 1199-7075 couples. Galvanic currents tended to stabilize after approximately 150 hours, at which time we refilled all cells with fresh electrolyte. Current flow increased markedly in the fresh solution before decaying to the same range reached prior to refilling. Galvanic couples of other cladding-core combinations gave similar results -- within $\pm 2 \times 10^{-4}$ milliamperes per sq cm -- after the current had stabilized, but different values initially and at the time of refilling.

During the test, several potential reversals occurred in the 5454-7075 galvanic cells. No reversals occurred in the other candidate-core cells. These tests indicate that any of the candidate alloys will protect alloy 7075, with the possible exception of alloy 5454.

General

None of the candidate alloys exhibited evidence of intergranular attack in the modified intergranular corrosion tests. Pitting of alloy 7040 in the cyclic acidified salt test showed an exfoliation tendency.

A review of results from all of the evaluations indicates that there are a number of specification alloys which offer promise as a cladding for 7075-T6. Some of these appear to be better than alloy 7072. In fact, alloy 7072 performed poorly in most of our tests. Only in the cyclic acidified salt test, a test generally used for assessing resistance to exfoliation attack, did 7072 have a higher corrosion resistance rating than most candidates.

PHASE II

Alloys 1199, 5457, 7472 and 7004 were selected from Phase I studies as the best potential cladding candidates. These alloys constituted the variables in Phase II -- the comparative evaluation of 7075 clad with the candidate alloys and 7075 clad with 7072.

SECTION VIII

MATERIALS

Alclad 7075 sheet was prepared with the cladding compositions of 1199, 5457, 7004, 7472 and 7072.

Clad composites were rolled to 0.036-inch and 0.090-inch thicknesses, then heat treated to produce the -T6 temper of 7075. Laboratory equipment was used for all rolling and heat treating. Desired cladding thicknesses were 4.0 % and 2.5 % for the 0.036-inch and 0.090-inch sheet, respectively. Actual thicknesses ranged from 2.6 % to 3.8% for 0.036-inch sheet, and from 1.6% to 2.2% for 0.090-inch sheet.

SECTION IX

PROCEDURE

Accelerated and Natural Environment Corrosion Tests

Finished stock in both thicknesses was used to prepare the same sample types used in Phase I. In addition, 1-inch by 6-inch samples were stressed into jigs (Figure 3). These samples were not intended to provide stress-corrosion data, but to evaluate the clad-core bond integrity. The stress level was approximately 17,000 psi, 25% of yield strength. We gained additional information on galvanic protection in all accelerated test environments by exposing the core at a cut near the apex of each stressed sample.

Surfaces were degreased to get a water-break-free surface prior to exposure in corrosion tests. Flat panels were coated on the top edges with a beeswax-resin mixture to prevent rundown of corrosion products from the exposed 7075. All samples were especially handled to avoid contamination of clean surfaces -- a practice requiring white glove treatment during assembly of lap joints.

Phase II incorporated the same accelerated corrosion tests and exposure periods described under Phase I. An additional exposure of 2000 hours was added to the 5% neutral salt spray test.

Limited availability of 7075 clad with alloy 7004 and 7472 required omission of certain test variables.

In addition to laboratory tests, we exposed flat panels, riveted joints, and bolted joints in natural atmospheres at Trentwood, Washington (industrial environment) and Daytona Beach, Florida (marine). Sample exposure was on standard frames inclined at 45 degrees. Removals are planned after one and two years' exposure.

Protective Value of Cladding

Solution potentials were measured on all composites in the manner described in Phase I. Both 0.036-inch and 0.090-inch stock were included to determine the influence of diffusion, through claddings of different thicknesses and compositions, on solution potential.

Both thicknesses of all composites were exposed for 100 hours in salt-peroxide solution (MIL-H-6088D, para. 4.4.3). Corroded areas from these samples were prepared for metallographic determinations of the type of attack encountered on each composite -- whether pitting or intergranular, and whether cladding protected the core.

The extent of diffusion was determined by electron microprobe analysis of all composites in both thicknesses, before and after heat treating to the -T6 temper. Scanning from the core alloy across the cladding thickness provided concentration gradients of Mg, Zn, and Cu as influenced by cladding alloy and thickness, and by the heat treatment for -T6 temper.

SECTION X

RESULTS AND DISCUSSION

Accelerated and Natural Environment Corrosion Tests

Corrosion and appearance ratings of panels exposed to 5% neutral salt spray are given in Figures 4 through 7. These ratings are representative of results from the other accelerated tests previously reported in detail (Ref 6). The cyclic acidified salt test caused more severe attack, whereas distilled water fog was relatively innocuous.

Claddings of alloys 1199 and 5457 provided consistently higher ratings than other alloys. Alloy 7072 gave the lowest performance rating, regardless of the way in which data were analyzed. Greater pitting susceptibility generally caused this lower rating for 7072, especially in cyclic acidified, and 5% neutral salt fog. Lack of pitting in distilled water fog raised the performance rating of 7072 in that particular test.

Natural environment exposures were initiated on January 23, 1967, at Trentwood, Washington, and on January 27, 1967, at Daytona Beach, Florida. Exposure time has not yet been long enough to permit meaningful comparison.

Protective Value of Cladding

Penetrometer measurements revealed no pit depths greater than the cladding thickness on the flat panels or in lap joints exposed to accelerated test environments.

Low power (30X) examination of stressed samples revealed some breakdown in protection to the core provided by alloys 5457 and 7004. Such attack occurred where the cladding had purposely been removed to expose the core (Figure 8). Significant attack of the 7075 core occurred only on samples exposed eight days in the cyclic acidified salt test.

Alloy 5457 generally afforded protection, but only as a result of preferential attack of a sub-surface layer. Similar preferential attack was noted on some 1199-clad stock, Figure 9, and occasionally with 7072 cladding. Preferential attack of this intermediate zone in the cladding occurred only on samples in the 2000-hour salt fog, and in the acidified salt spray tests. It was most severe on 5457-clad 7075 -- causing pronounced blistering of the clad surface in cyclic acidified salt fog (Figure 10).

No cladding delamination was noted on any of the stressed samples and the stress had no effect on corrosion performance.

Microprobe data provided excellent resolution of composition gradients for the major alloying elements present in the 7075 core -- zinc, magnesium and copper. These data are typified in the concentration profiles for 1199-clad 7075 shown in Figure 11. (Complete microprobe data are reported in Reference 7.)

The solution heat treatment caused significant diffusion. At the 0.036-inch sample surface, the 1199 alloy cladding contained as much zinc as that nominally found in alloy 7072.

A comparison of concentrations of these various elements on 0.036-inch and 0.090-inch sheet revealed that:

1. Concentrations at equal distances from the clad-core interface were similar for the same element.

2. Concentrations decreased as the distance from the interface increased.

3. Cladding composition did not significantly influence diffusion of copper.

These expected observations support the use of thicker cladding to reduce diffusion to the surface by such detrimental elements as copper.

We believe that solution potentials of the clad composites support the microprobe data, Table III. Potential values for 0.090-inch sheet are consistently more electronegative than those for 0.036-inch sheet. We attribute this difference in potentials to the higher copper concentration at the surface of 0.036-inch sheet -- further support for greater cladding thickness.

General

Consideration of corrosion rating data indicates the relative performance of cladding alloys to be (in order of decreasing merit):

1199
5457
7004
7472
7072

No one alloy offers the best corrosion resistance as well as the best galvanic protection, however. Further development presents the alternative of (a) a cladding with acceptable surface corrosion resistance along with mechanical properties equivalent to the core alloy, or (b) one having maximum surface corrosion resistance but providing no strength to the composite.

A cladding composition offering excellent mechanical properties represents a complex alloy system. Diffusion of certain elements from the core can further complicate the mechanical and electrochemical characteristics of a heat-treatable cladding alloy. While the goal is extremely attractive, it will not be reached without extensive alloy development. Less complex would be the development of a non-heat-treatable alloy with better corrosion resistance than 7072. Such a cladding alloy could be used, not only for 7075, but for a range of alloys.

SECTION XI

STATUS

The principal effort under laboratory evaluation of cladding alloys for 7075-T6 has been completed. Panels being maintained in natural environment exposures will be recalled for evaluation after one year's exposure. No major effort is scheduled before return of those samples.

SECTION XII

REFERENCES

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2. B. W. Lifka and D. O. Sprowls, "An Improved Exfoliation Test for Aluminum Alloys", Corrosion , 22 (1), pp 7-15 (1966).

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5. Thomas A. Lowe, Corrosion-Resistant Cladding for 7075-T6: Phase I, MS PR 66-71, August 12, 1966.

6. Thomas A. Lowe, Corrosion-Resistant Cladding for 7075-T6: Phase II, MS PR 67-27, March 16, 1967.

7. Monthly Letter Report (March 1, 1967 to April 1, 1967), April 13, 1967.

TABLE I

COMPOSITION OF CLADDING CANDIDATES

(MAJOR ALLOYING ELEMENTS) *

	Per Cent by Weight		
Alloy	Mg	Zn	Other
1199	0.002	0.000	---
5457	0.91	0.000	0.20 Mn
5454	2.71	0.03	0.83 Mn
6253	1.15	2.04	0.63 Si
7004	1.68	4.40	---
7040	3.52	3.57	0.25 Mn
7472	1.18	1.56	---
7272	0.0008	2.49	---
7072	0.0007	1.12	---

* Balance is aluminum.

TABLE II

CLADDING CANDIDATE SOLUTION POTENTIALS[1]

Alloy	Volts 2 hr	Volts 6 hr
1199-T6[2]	-0.840	-0.850
5457-T6	-0.827	-0.813
5454-T6	-0.800	-0.801
6253-T6	-0.950	-0.951
7004-T6	-0.929	-0.929
7040-T6	-0.900	-0.905
7472-T6	-0.968	-0.972
7272-T6	-1.013	-1.015
7072-T6	-0 948	-0.951
7075-T6 (core alloy)	-0.790	-0.790

(1) 0.1 N Calomel reference in a solution of 53 g/l NaCl and 3 g/l H_2O_2, 25C.

(2) All cladding candidates were heat treated in the manner required to provide the -T6 temper for alloy 7075.

TABLE III

SOLUTION POTENTIALS OF CLADDING-7075-T6 COMPOSITES*

Cladding Alloy	Volts			
	2 hr		6 hr	
	0.036 in.	0.090 in.	0.036 in.	0.090 in.
1199	-0.86	-0.90	-0.86	-0.91
5457	-0.84	-0.85	-0.85	-0.86
7004	-0.92	-0.98	-0.92	-0.98
7472	-0.90	-0.94	-0.89	-0.94
7072	-0.91	-0.92	-0.90	-0.92

* 0.1 N Calomel reference in a solution of 53 g/l NaCl and 3 g/l H_2O_2, 25C.

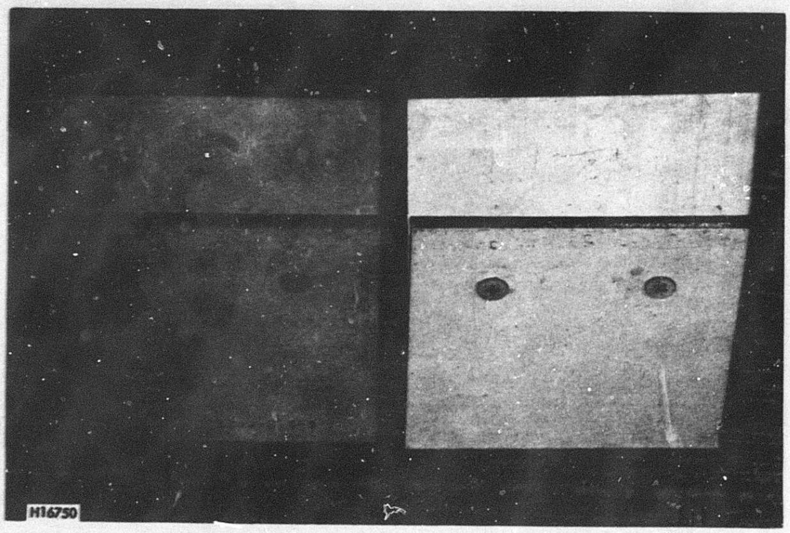


Figure 1. Lapped-Joint Test Samples

Panels with aluminum rivets, left, or cadmium-plated steel fasteners, right, were installed in all test environments with the crevice facing up to facilitate moisture penetration into the lap.

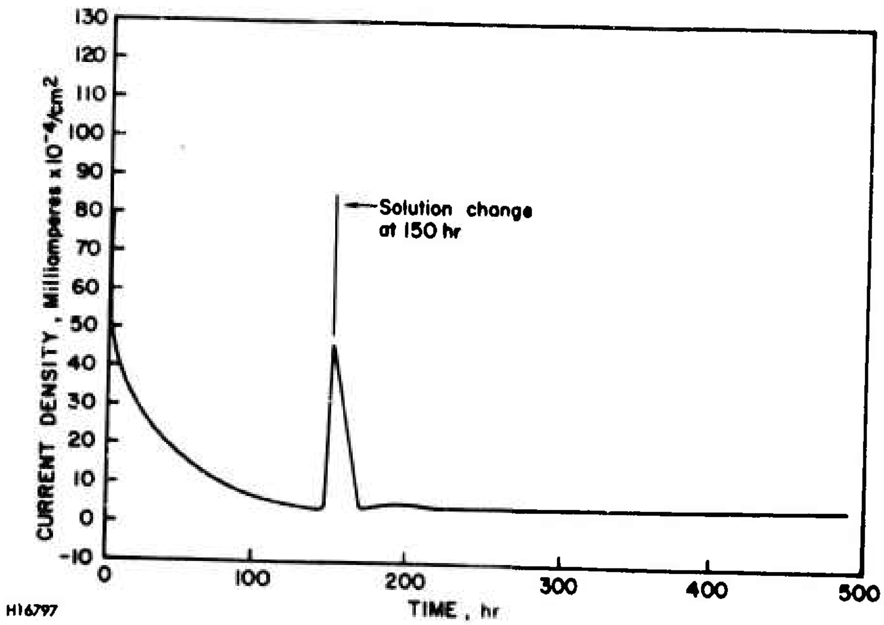


Figure 2. Current Density-Time Relationship of 1199-7075-T6 Galvanic Couple

Fresh 3% NaCl electrolyte was placed in the cell after 150 hours. All cladding candidates provided galvanic performance similar to that indicated here.

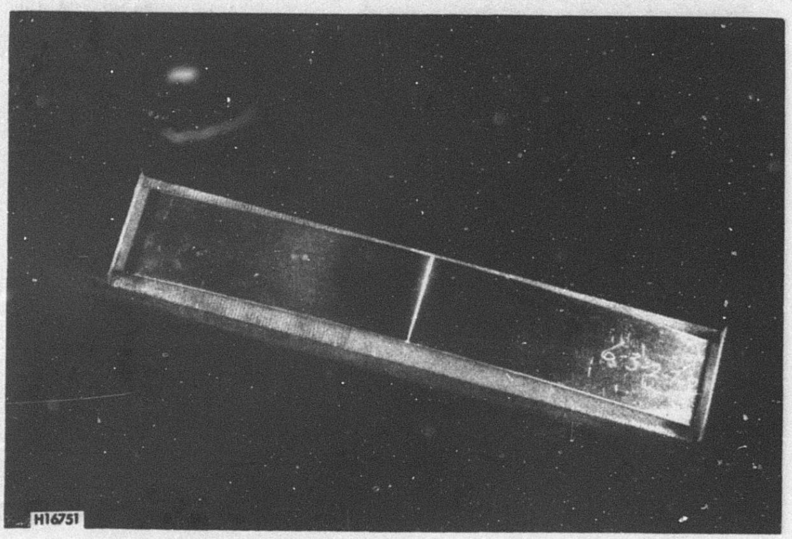


Figure 3. Stressed Sample Configuration

The core alloy was exposed by cutting through the cladding at the bend apex.

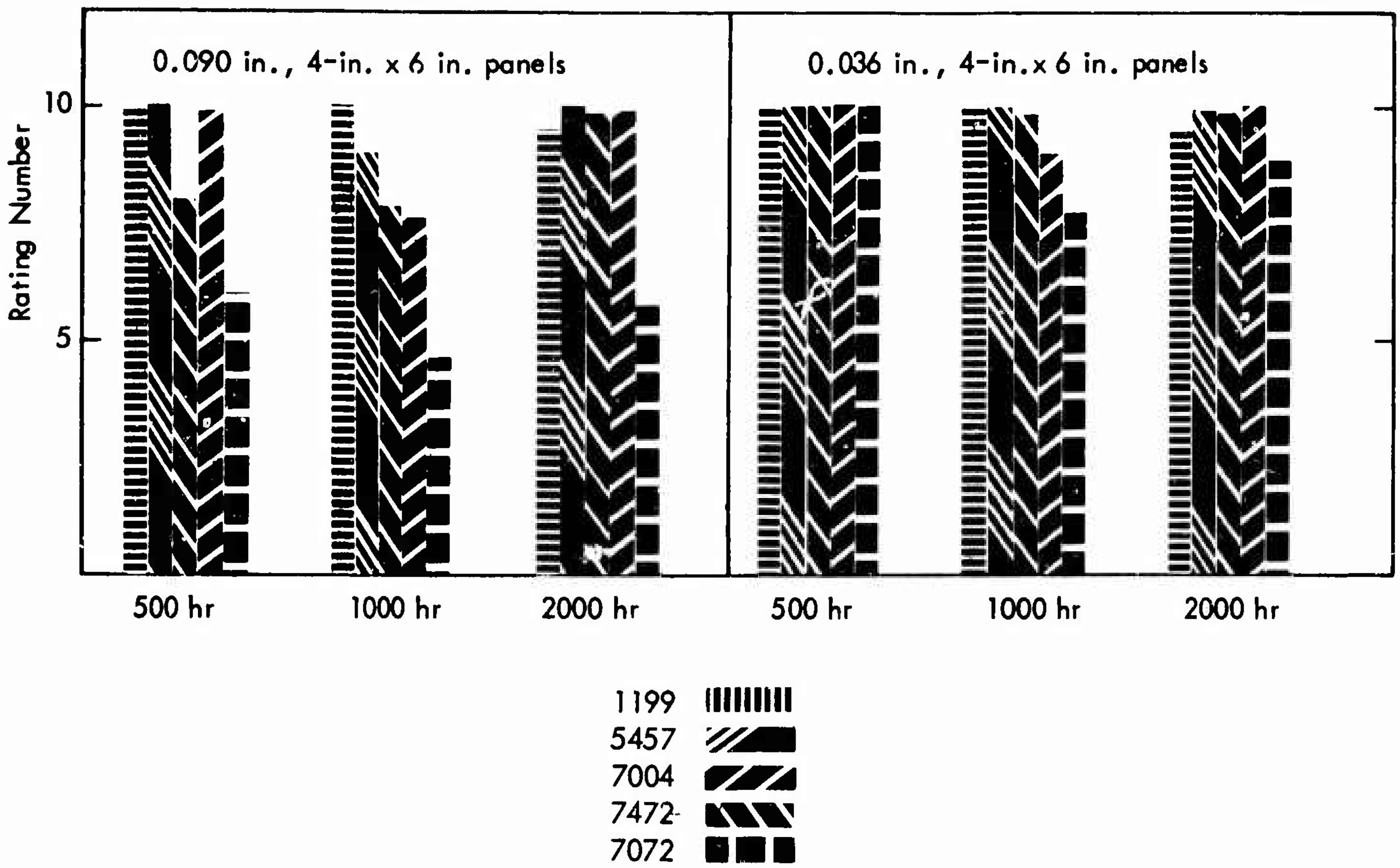


Figure 4. Corrosion Rating of Flat Panels

Ratings made of clad composites after exposures up to 2000 hours in 5% neutral NaCl fog. Cladding alloy is identified in the legend.

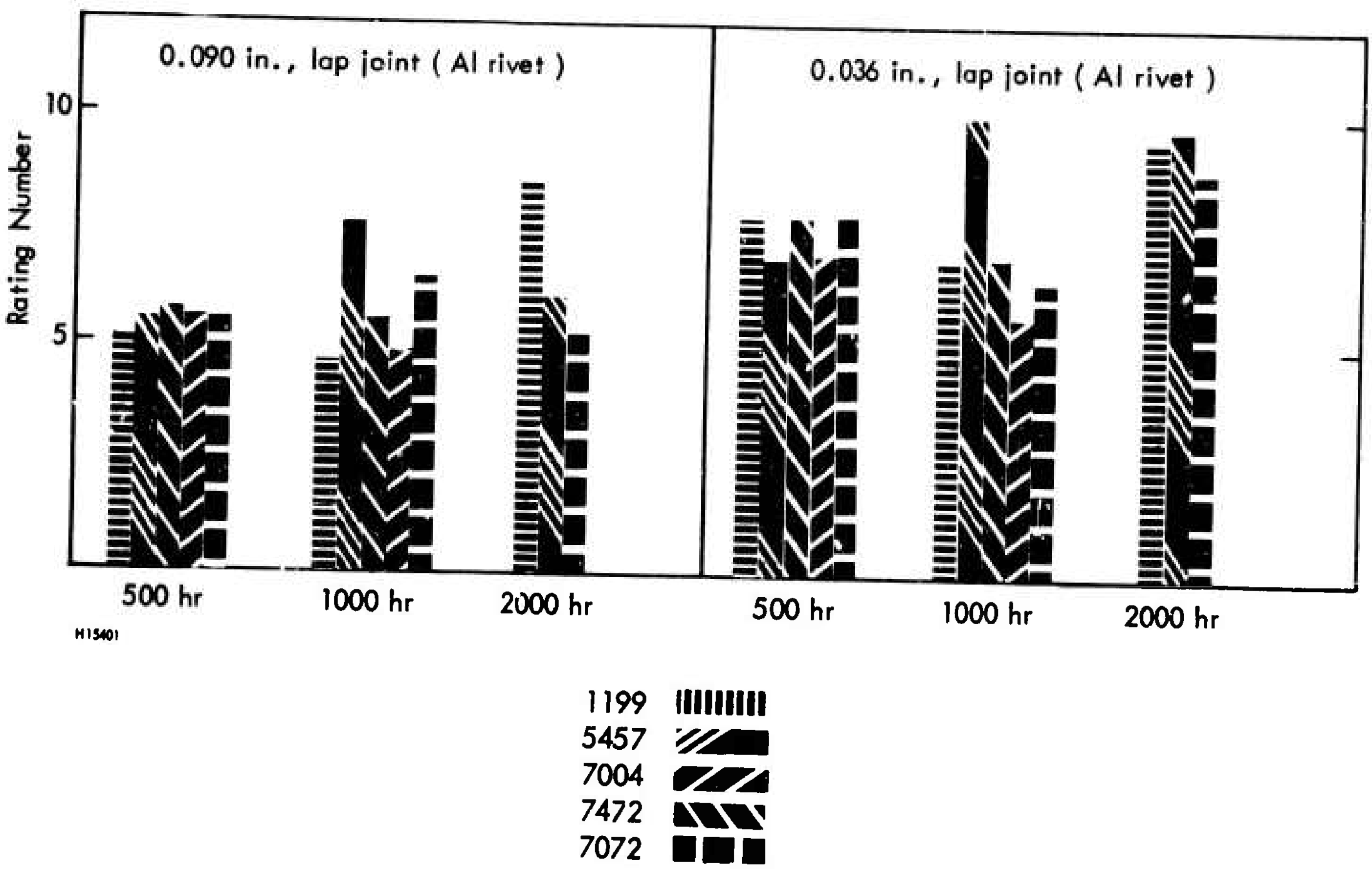


Figure 5. Corrosion Rating of Riveted Lap Joints

Ratings made of clad composites after exposures up to 2000 hours in 5% neutral NaCl fog. Cladding alloy is identified in the legend.

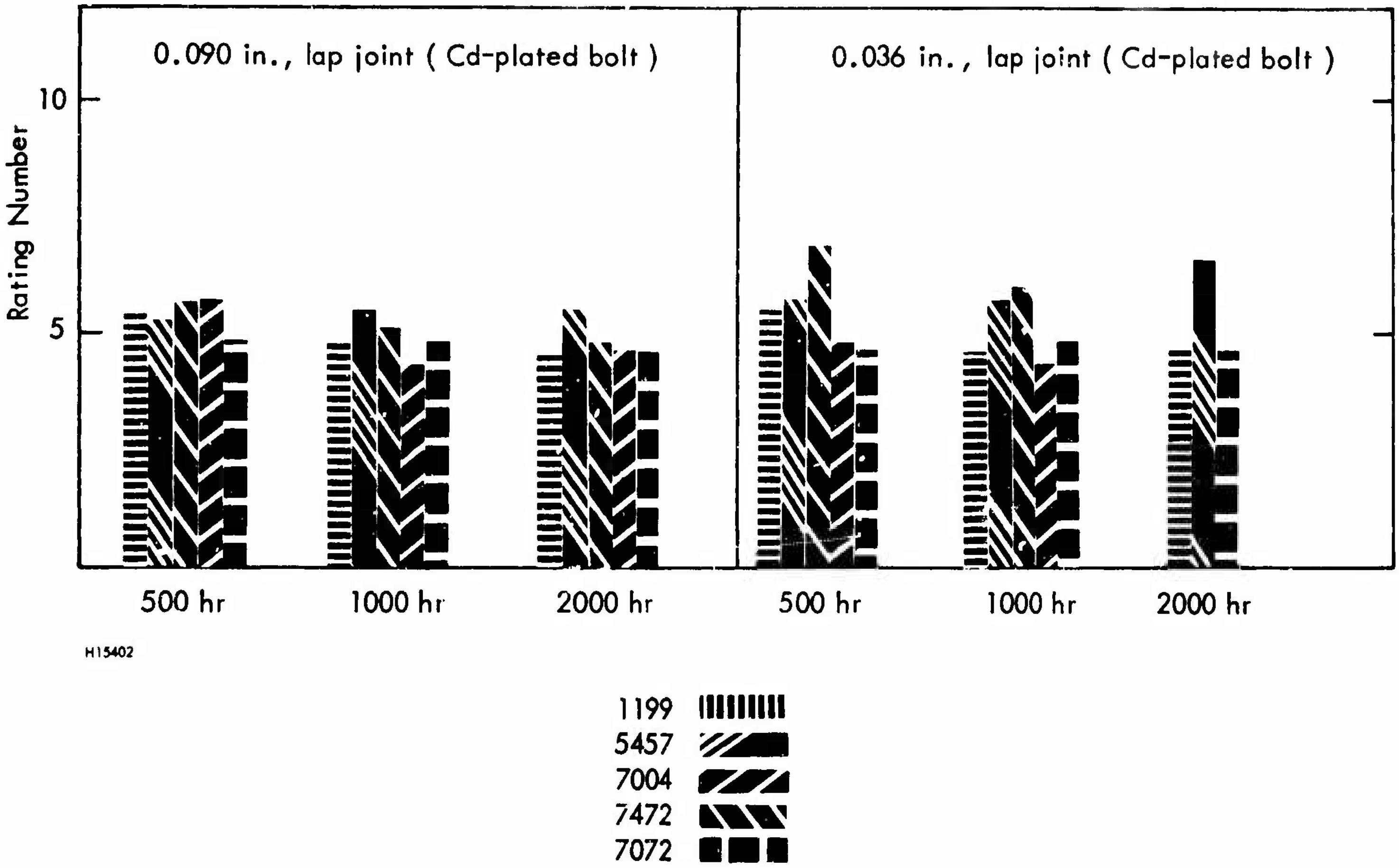


Figure 6. Corrosion Rating of Bolted Lap Joints

Ratings made of clad composites after exposures up to 2000 hours in 5% neutral NaCl fog. Cladding alloy is identified in the legend.

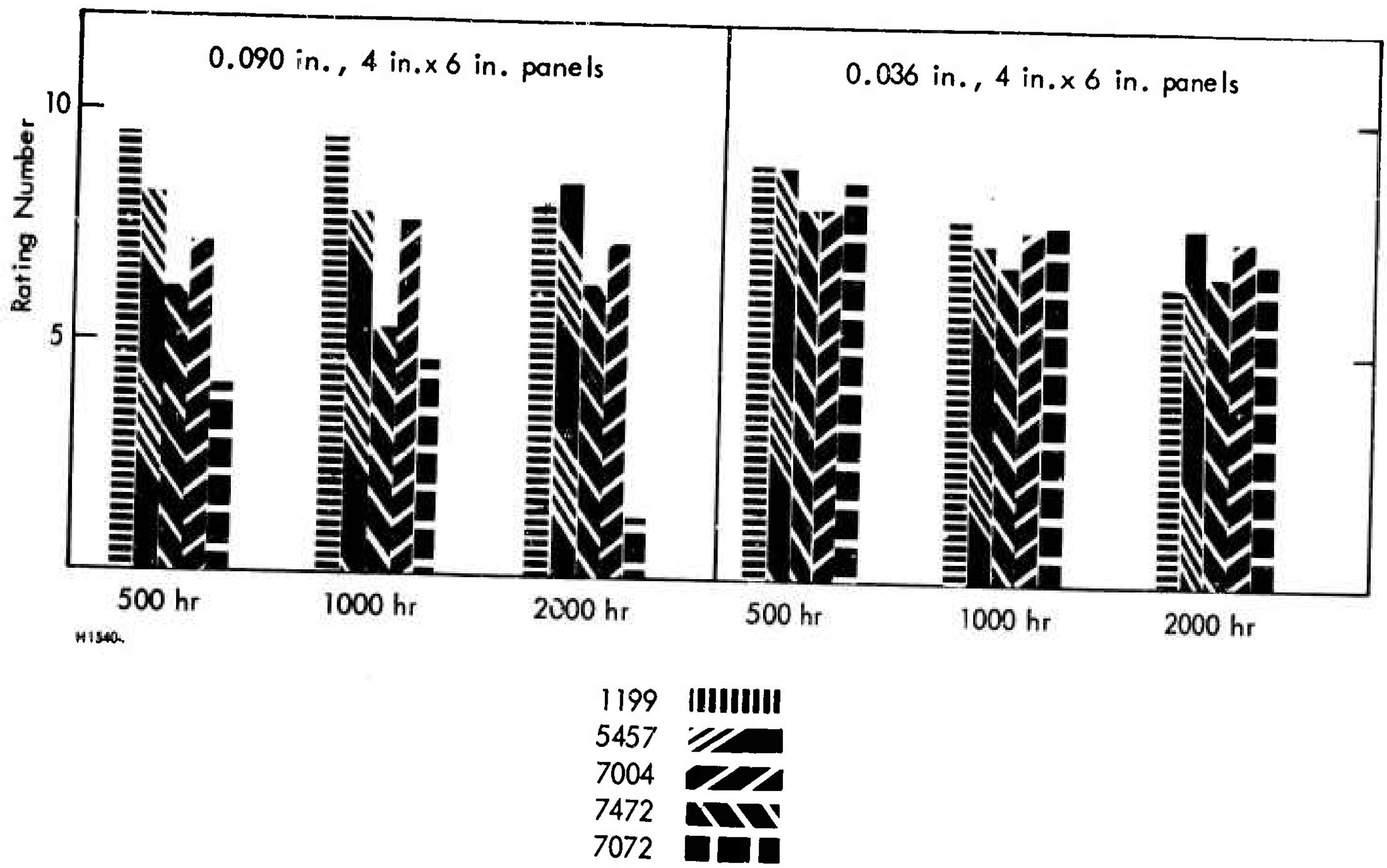
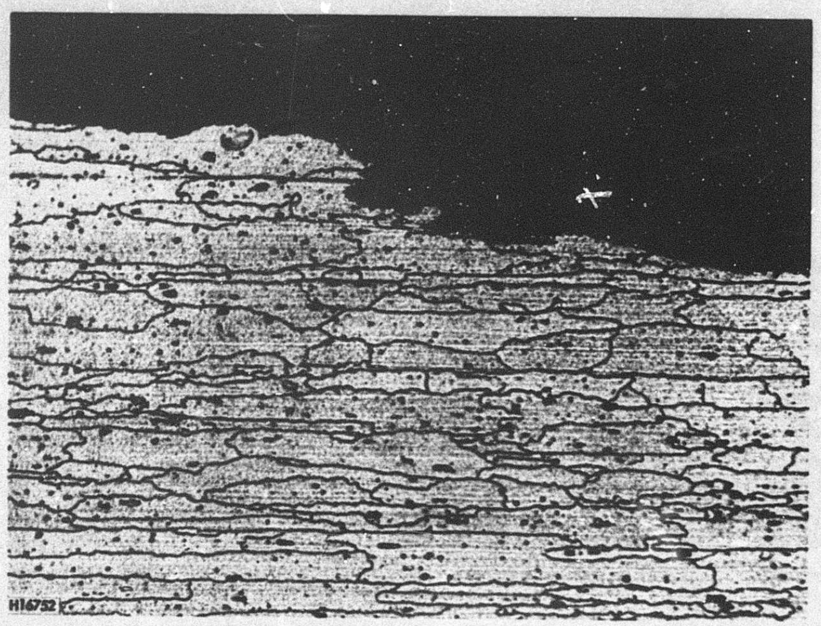


Figure 7. Appearance Rating of Flat Panels

Ratings made of clad composites after exposures up to 2000 hours in 5% neutral NaCl fog. Cladding alloy is identified in the legend.

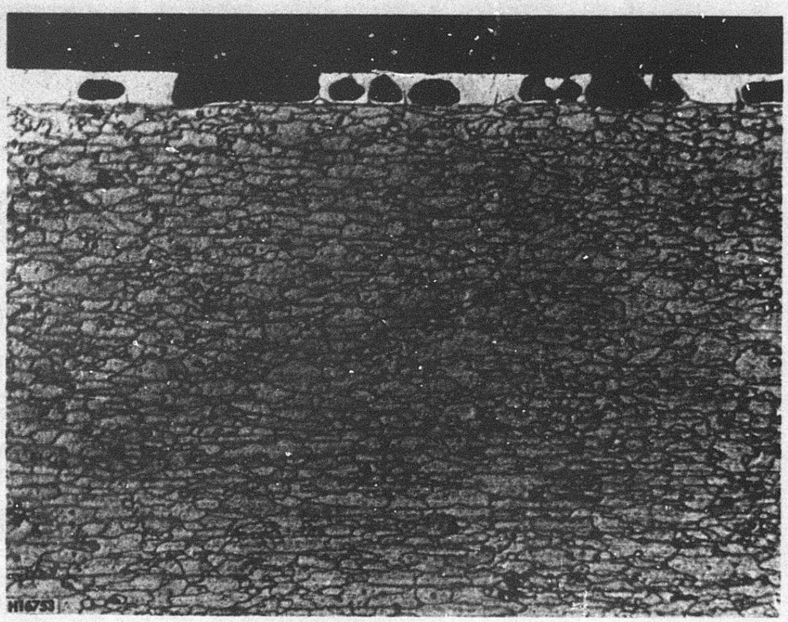
Clad
Core
Interface



Chromic Etch, 45 sec. 180F 200X

Figure 8. Cladding Failure to Protect the Core Alloy

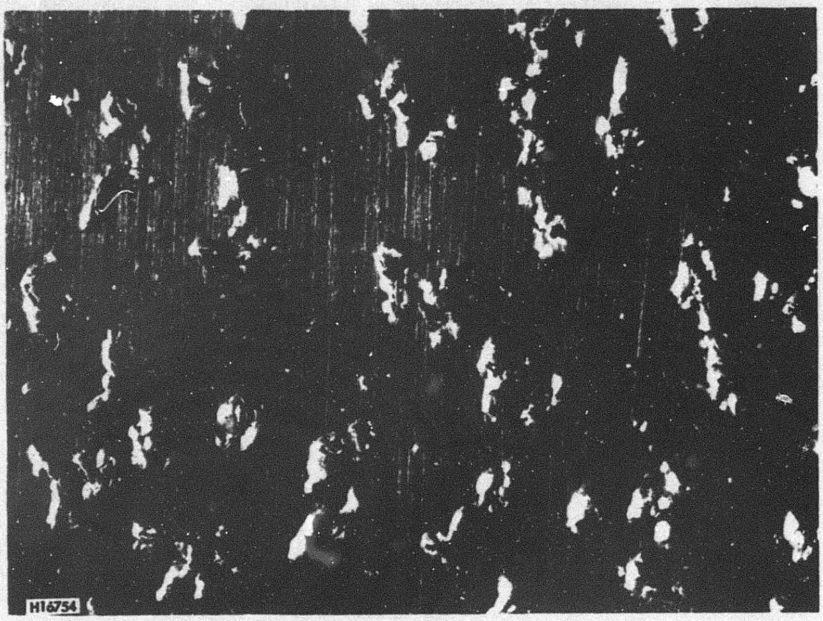
Slight attack of the 7075 core is seen on this section from 5457-clad 7075. The section was removed from an 0.090-inch stressed sample at the milled damage mark. This attack occurred after a 192-hour exposure in the cyclic, acidified salt fog test.



Chromic Etch - 45 sec. 180F 200X

Figure 9. Preferential Attack of a Sub-Surface Layer on 1199-Clad 7075

This section was removed from an 0.036-inch sample exposed for 196 hours in the cyclic, acidified salt fog test.



5X

Figure 10. Surface Blistering of 5457 Cladding

Such blistering occurred only on 5457-clad samples exposed in the cyclic, acidified salt fog test.

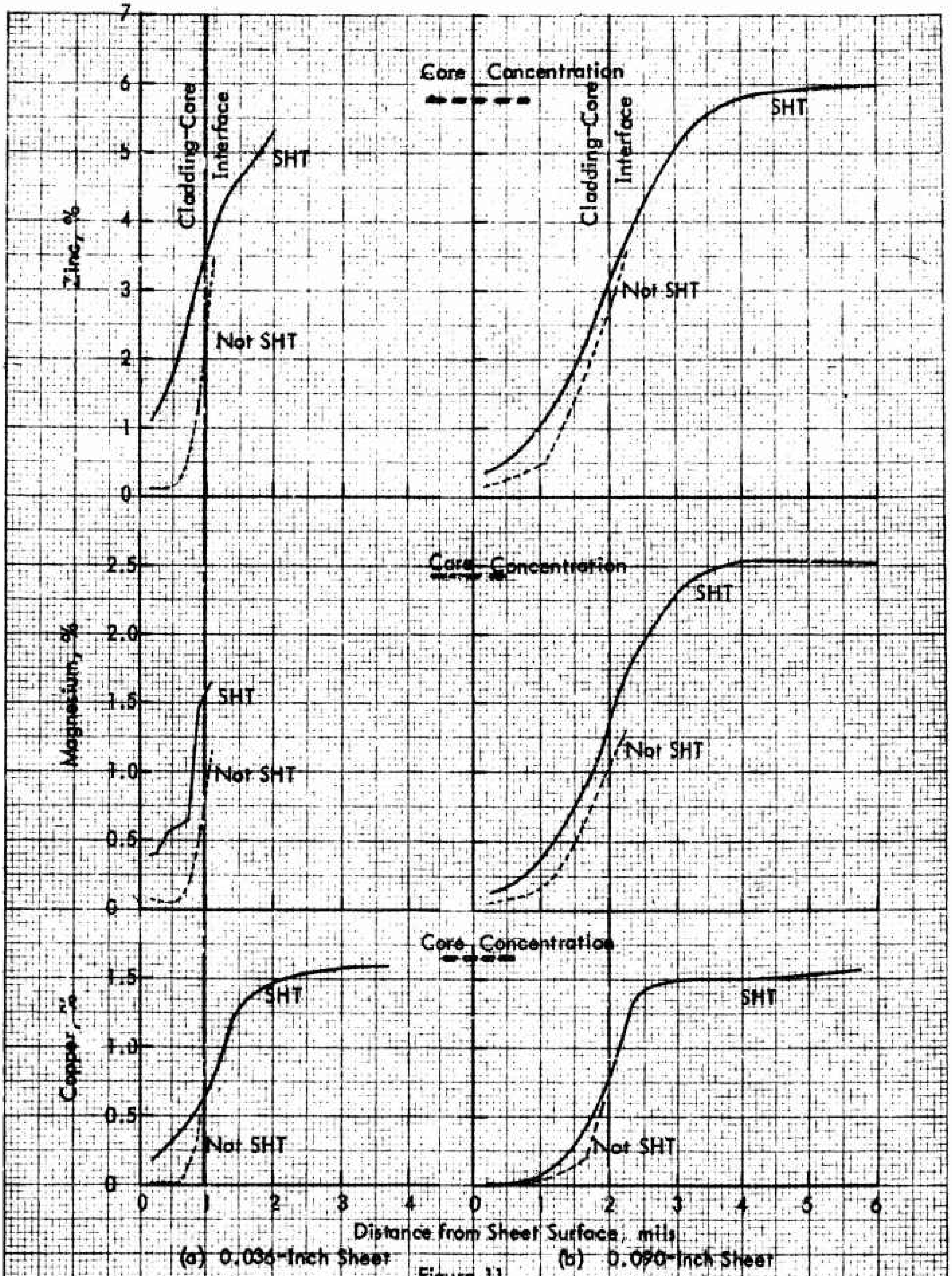


Figure 11

COMPOSITION PROFILES NEAR SURFACE OF 1199-CLAD 7075 SHEET (SAMPLE SERIES NO. 1)
Profiles are shown for both the solution-heat-treated (SHT) and not-solution-heat-treated (Not SHT) samples. Bold dashed lines designate the concentration of each element as determined by wet chemical analysis. The approximate cladding-core interface is also shown for each sample gauge.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Kaiser Aluminum & Chemical Corporation Department of Metallurgical Research Spokane, Washington	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

Corrosion Resistant Cladding For 7075 T6 Aluminum Alloy

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

First annual Summary Report June 1966 to May 1967

5. AUTHOR(S) (Last name, first name, initial)

Lowe, Thomas A.

6. REPORT DATE	7a. TOTAL NO. OF PAGES 27	7b. NO. OF REFS

8a. CONTRACT OR GRANT NO. AF33(615)-3939 b. PROJECT NO. 7381 c. Task No. 738107 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-67-319 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Research and Technology Division Air Force Systems Command, USAF

13. ABSTRACT

By contractor.

Corrosion of ~~Alclad~~ clad 7075 aircraft alloy prompted the Air Force to sponsor an evaluation of different cladding compositions. The objective was to determine if these compositions offered better corrosion resistance than 7072, while providing adequate galvanic protection.

Accelerated corrosion tests indicate that there are registered aluminum alloys that offer an improvement over 7072. Further work is needed to optimize a composition.

DD FORM 1 JAN 64 1473 Attch 3

Unclassified

Security Classification

H16798

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Aluminum Alloys Composites, Aluminum Cladding, Aluminum Alclad						

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